FORCES BETWEEN SURFACES WITH SURFACE-SPECIFIC INTERACTIONS IN A DILUTE ELECTROLYTE

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We have investigated the forces between two surfaces, immersed in a dilute electrolyte solution, interacting specifically with the ions that are in their immediate vicinity. It is found that at large separations the free energy decays exponentially (the decay length being approximately half the Debye length) with separation, while the magnitude of the force depends on the physical properties of the surfaces and their interactions with the nearby ions. This long-range attractive force could well represent a case for the electrostatic nature of the surface-specific very long-range "hydrophobic" interaction.

1. Introduction

Recently [1] considerable effort has been directed towards understanding of forces between surfaces bearing laterally mobile charges interacting across a medium described solely by its dielectric constant. In this contribution we have analysed the forces between surfaces with which the charges can interact specifically while interacting electrostatically through the intervening medium, an uni–uni valent electrolyte of known ionic strength and dielectric constant. This system is in many respects similar to those studied before [1] but also exhibits features that were previously not adequately percieved.

We supposed (fig. 1) that in the immediate vicinity of the two originally uncharged surfaces separated by $2a$ and located at the points of dielectric discontinuities $z = \pm a$, where z is the coordinate axis perpendicular to the surfaces, there is a regime of space of transversal dimension ζ where mobile charges of both signs experience specific interactions with the surface, with energies E^+ and E^-, respectively. These short-range interactions can model the changed local aqueous environment brought by the hydrophobic nature of the sur-

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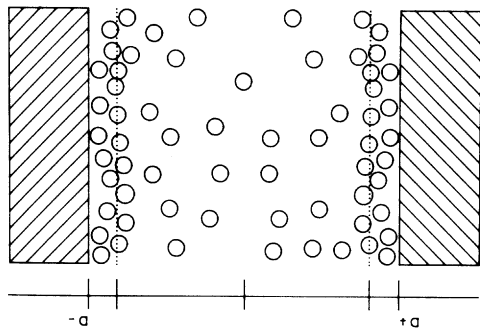[1] On leave from J. Stefan Institute, Ljubljana, Yugoslavia.

Fig. 1. Two interacting surfaces at separation $2a$. The regions close to the surfaces, where ions experience specific interactions with the surfaces, are delimited by the dotted line. These specific interactions are presumably related to the modified solvent structure as a consequence of the hydrophobic nature of the surfaces. If the extent of this region is small enough compared to intersurface separation, we can assume that only the surface energy of the system is perturbed by the interactions.

faces. To make the model analytically tractable we took the limit $\zeta \to 0$ [#1]. This limit furthermore implies that specific interactions are limited to the surfaces at $z = \pm a$, therefore contributing only to the surface free energy of the system. The ionic density fluctuations due to specific interactions of ions with the surface, limited only to the space near the surface could well be the cause of the "long-range hydrophobic interactions" as argued recently [2].

In our analysis of the problem we took advantage of the recently introduced [3] extended Poisson–Boltzmann approximation. It consists of a transformation by means of which it is possible to write the grand canonical partition function in terms of a functional integral over local electrostatic potentials. We developed the action of the integral up to second order in terms of local electrostatic potential in the vicinity of its mean-field (Poisson–Boltzmann) value. The thermodynamic potential derived from the functional integral representation of the partition function will decouple into two terms: the mean-field and the fluctuation part. The latter was investigated in the asymptotic regime of large intersurface separations.

2. Analysis

Our system is composed of $2N$ mobile monovalent charges of both signs, occupying the space $|z| \leqslant \infty$. As stated above the specific interactions between the mobile ions and the surfaces, presumably localised in the vicinity of the surfaces, were assumed to occur only at $z = \pm a$. The dielectric constant in the whole region of interest was taken as ϵ (the image effects will therefore not be dealt with). The grand canonical partition function in the form of a functional integral was derived in detail in ref. [3]:

$$\Xi = \frac{(2\pi\beta)^N}{[\det u(\mathbf{r}, \mathbf{r}')]^{1/2}} \int_{(2N)} \cdots \int \exp\left(-\frac{S(ie_0)}{kT}\right) d\varphi(\mathbf{r}_1) \ldots d\varphi(\mathbf{r}_{2N}), \tag{1}$$

where $\det u(\mathbf{r}, \mathbf{r}')$ is the functional determinant of the electrostatic interaction potential $u(\mathbf{r}, \mathbf{r}')$, $\varphi(\mathbf{r})$ is the local value of electrostatic potential, β is the thermal energy ($\beta^{-1} = kT$), and e_0 is the electron charge. The action S is given by

$$S(e_0) = \tfrac{1}{2}\epsilon\epsilon_0 \int (\operatorname{grad} \varphi)^2 \, d^3\mathbf{r} + kT \int 2z_a \operatorname{ch}(\beta e_0 \varphi(\mathbf{r})) \, d^3\mathbf{r} + \int f(\varphi) \, d^2\mathbf{r}, \tag{2}$$

with z_a the bulk activity of the ions and ϵ_0 the permittivity of vacuum. We have not explicitly written down the surface part of the free energy $f(\varphi)$. If there are no specific interactions at the surface, then $f(\varphi) = \sigma\varphi$, as shown in ref. [3], where σ is the surface charge density. In the case of specific interaction with energies E^+ and E^- we can derive the form

$$f(\varphi) = kTn_s \ln[1 + z_s^+ \exp(-e_0\varphi/kT)] + kTn_s \ln[1 + z_s^+ \exp(e_0\varphi/kT)],$$

with n_s being the surface density of the interaction sites while $z_s^\pm = \exp(-E^\pm/kT)$. In what follows we did not limit ourselves to any particular form of the surface part of the energy density, leaving our analysis as general as possible.

Since the action in eq. (1) is non-linear, no closed analytical expression is available for Ξ. However, a reasonably good approximation scheme proposed recently [3] consists in developing the non-linear action up to the second order in the deviations of $\varphi(\mathbf{r})$ from its mean-field (i.e. Poisson–Boltzmann) value, determined by the stationary value of the action, i.e.

$$S = S(\varphi_{PB}(z)) + \frac{1}{2} \int \left. \frac{\partial^2 S}{\partial\varphi(\mathbf{r})\,\partial\varphi(\mathbf{r}')} \right|_{\varphi_{PB}(z)} \delta\varphi(\mathbf{r})\,\delta\varphi(\mathbf{r}') \, d^3\mathbf{r} \, d^3\mathbf{r}', \tag{3}$$

[#1] The meaning of this limit is that ζ is much smaller than the intersurface separation $2a$.

where $\varphi_{PB}(z)$ is obtained from

$$\partial S/\partial\varphi(r)|_{\varphi_{PB}(z)} = 0. \tag{4}$$

The above condition is easily seen to lead to the standard Poisson–Boltzmann equation in the planar geometry (depending only on the z coordinate), plus a boundary condition of a charge regulation type [4] depending on the form of the surface part of the free energy $f(\varphi)$. The grand canonical partition function can be therefore reduced to the Gaussian integrals that can be, at least in principle, evaluated exactly.

We shall not give details of the derivation. The final expression for the thermodynamic potential, defined as $\Omega = -kT \ln \Xi$, is obtained as a sum of two terms. The first one is nothing but the mean-field free energy, given by the standard form as the energy per unit surface area (A),

$$\frac{\Omega}{A} = -\tfrac{1}{2}\epsilon\epsilon_0 \int \left(\frac{\partial\varphi_{PB}}{\partial z}\right)^2 dz - kT \int 2z_a \, \mathrm{ch}(\beta e_0\varphi_{PB}) \, dz - f(\varphi_{PB}). \tag{5}$$

φ in the above equation is nothing but the Poisson–Boltzmann solution depending only on the transversal coordinate (z).

The other part of the thermodynamic potential, corresponding to the fluctuations of the electrostatic potential around its mean-field value (evaluated in the harmonic approximation, cf. eq. (3)), can be obtained [3] in the form of a coupling constant integral

$$\Omega_F = \tfrac{1}{2}kT \int_0^{\beta e_0^2} d\mu \, \mathrm{Tr}[\rho(r') R_\mu(r,r') + 2\rho_s(a) \, \delta(z-a) \, R_\mu(r,r')], \tag{6}$$

where Tr is the trace operator, $\delta(r)$ is the Dirac delta function, $\rho(r)$ is the local charge density $\rho(r) = \rho(z) = 2z_a \, \mathrm{ch}(e_0\beta\varphi_{PB}(z))$, μ the coupling parameter and

$$\rho_s(a) = -(kT/e_0^2) \, \partial^2 f/\partial\varphi^2|_{\varphi_{PB}}. \tag{7}$$

The Green function $R_\mu(r,r')$ is obtained as the solution of

$$\epsilon\epsilon_0\nabla^2 R_\mu(r,r') - \mu\rho(r) R_\mu(r,r') = -\delta(r-r'), \tag{8}$$

with the boundary condition at the walls of the form (with $\delta \to 0$)

$$\epsilon\epsilon_0 \, \partial R_\mu/\partial z|_{+a-\delta}^{+a+\delta} = \mu\rho_s(a) R_\mu(a) \tag{9}$$

with $a \to -a$ for the other wall. The solution of eq. (8) can be obtained straightfowardly in the WKB approximation, as discussed in ref. [3]. Since we only need $R_\mu(r,r)$ to evaluate the free energy due to the fluctuations we can derive

$$R_\mu(r,r) = \int_0^\infty r_\mu(Q; z, z) \, Q \, dQ, \tag{10}$$

with

$$r_\mu(Q; z, z) = \frac{1}{2\epsilon\epsilon_0 u(z)} \left(1 + \frac{2\alpha \exp[-2\Delta(a)]}{1-\alpha^2 \exp[-2\Delta(a)]} \{\exp[\Delta(a)] \, \mathrm{ch} \, \Delta(z) + \alpha\}\right), \tag{11}$$

where the following abbreviations were used

$$u^2(z) = Q^2 + L\rho(z), \tag{12a}$$

$$\Delta(z) = \int_{-z}^{z} u(z') \, dz', \tag{12b}$$

$$\alpha = \tfrac{1}{2} L\rho_s(a) / [2u(a) + \tfrac{1}{2} L\rho_s(a)], \tag{12c}$$

and $\rho(z)$ is again the charge density obtained through the solution of the Poisson–Boltzmann equation with the appropriate boundary conditions.

Calculation of the coupling integral, eq. (6), is tedious. The final result is

$$\Omega_F = \frac{kT}{12\pi} \int_{-a}^{a} [L\rho(z)]^{3/2} \, dz + \frac{kT}{12\pi} \int_{0}^{\infty} Q \, dQ \left[\ln\{1 - \alpha^2 \exp[-2\Delta(a)]\} - \ln(1 - \alpha^2) + \ln\left(1 + \frac{L\rho_s(a)}{2Q}\right) \right], \tag{13}$$

where $L = e_0^2/kT\epsilon\epsilon_0$. As shown before [3] in all the divergent Q integrals in eq. (13) the upper limit should be substituted with $1/b$, where b is the radius of the ions. This procedure approximately accounts for the short-range repulsion that was not included explicitly in our calculations thereby insuring the stability of the Coulomb system.

3. Results

We do not dwell on the overall dependence of the fluctuation part of the free energy on the intersurface separation, but do analyse only the asymptotic regime $a \to \infty$.

In the asymptotic limit we have approximately

$$\lim_{a \to \infty} \Delta(a) \approx 2a\sqrt{Q^2 + \kappa^2}, \tag{14}$$

where $\kappa = \sqrt{L z_a}$ is the standard inverse Debye length. It is evident that only the second term in eq. (13) contributes significantly to the a dependence of Ω_F in this particular limit. In fact we can derive the following limiting form,

$$\Omega_F \approx \frac{kT}{4\pi} [\tfrac{1}{2} L\rho_s(a)]^2 \int_{0}^{\infty} Q \, dQ \, \frac{\exp[-2\Delta(a)]}{Q^2 + L\rho(a)}, \tag{15}$$

where we have made an additional assumption that in the $a \to \infty$ limit we have $\sqrt{L\rho(a)} \gg \tfrac{1}{2} L\rho_s(a)$. This assumption basically amounts to the statement that in a dilute electrolyte the electrostatic screening length right at the surface is the smallest length involved in the problem. The difference between the surface and bulk electrostatic screening is of course a consequence of the specific interactions at the bounding surfaces.

Introducing the substitution $u^2 = Q^2 + L\rho(a)$, we are finally led to the following asymptotic expression

$$\Omega_F = \frac{kT}{4\pi} [\tfrac{1}{2} L\rho_s(a)]^2 \int_{\sqrt{L\rho(a)}a}^{\infty} \frac{du \exp[-2\Delta(u)]}{u} \approx \frac{kT}{4\pi} [L\rho_s(a)]^2 \frac{\exp(-4\kappa a)}{\sqrt{L\rho(a)}\, a}. \tag{16}$$

The dependence of the free energy on the intersurface separation is given by the exponential function, its magnitude, however, depends on the parameters describing the surface and determining the values of $\rho_s(a)$ and $\rho(a)$. The above result basically tells us that the interactions between the two surfaces, due to the fluctuations in the local charge density in the vicinity of the surfaces, are screened with half the Debye length in between the surfaces and with the decay length $\approx 1/\sqrt{L\rho(a)}$ along a single surface.

Recently [2] we have been able to fit the data on the very long-range "hydrophobic" forces acting between hydrophobized mica or silica surfaces [5,6] to a form basically identical to that of eq. (16) in the same asymptotic limit. The effective ionic strength of the medium obtained from the fitted decay rate of the free energy

turns out to be on the order of $\approx 10^{-5}$ M, and is probably due to the ionic impurities present in the "conductivity" water in which the measurements have been performed. On the other hand, for the experimental cases where the ionic strength was known [7], the values of the Debye length obtained from the fit are in perfect agreement with those computed on the basis of experimental ionic strengths.

The forces due to the fluctuations in the local charge density at the surface described above therefore seem to be a promising candidate to explain the long-range attraction between hydrophobized surfaces. An expanded version of this report will be published elsewhere [8].

Acknowledgement

References

[1] P. Attard, R. Kjellander, D.J. Mitchell and B. Jönsson, J. Chem. Phys. 89 (1988) 1664.
[2] R. Podgornik, D.C. Rau and V.A. Parsegian, Nature, submitted for publication.
[3] R. Podgornik and B. Žekš, J. Chem. Soc. Faraday Trans. II 84 (1988) 611.
[4] B.W. Ninham and V.A. Parsegian, J. Theoret. Biol. 31 (1971) 405.
[5] H.K. Christensson and P.M. Claesson, Science 229 (1988) 390.
[6] Ya.I. Rabinowich and B.V. Derjaguin, Colloids Surfaces 30 (1988) 243.
[7] H.K. Christensson, P.M. Claesson, J. Berg and P.C. Herder, J. Phys. Chem., in press.
[8] R. Podgornik, manuscript in preparation.
[9] J. Mahanty and B.W. Ninham, Dispersion forces (Academic Press, New York, 1976).